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(Statement A)

## Improved Synthesis of $\text{CsN}_3$

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*Dedicated to Professor Joachim Straehle on the occasion of his 65<sup>th</sup> birthday*

**Abstract.** Cesium azide can conveniently be prepared from anhydrous  $\text{CsF}$  and  $(\text{CH}_3)_3\text{SiN}_3$  in  $\text{SO}_2$  solvent in high purity and yield. In this reaction, the initially generated  $\text{SO}_2\text{F}^-$  anion is converted in  $\text{SO}_2$  solvent to solvated azide,  $(\text{SO}_2)_n\text{N}_3^-$ , which is labile and releases  $\text{SO}_2$  under dynamic vacuum yielding pure  $\text{CsN}_3$ .

**Keywords:** Cesium azide; Fluorosulfite; Azidosulfite

## Verbesserte Synthese von $\text{CsN}_3$

**Inhaltsübersicht.** Cäsiumazid kann bequem durch die Reaktion of wasserfreiem  $\text{CsF}$  und  $(\text{CH}_3)_3\text{SiN}_3$  in  $\text{SO}_2$  Lösung in hoher Reinheit und Ausbeute dargestellt werden. In dieser Reaktion wird das zuerst gebildete  $\text{SO}_2\text{F}^-$  Anion in  $\text{SO}_2$  Lösung zu dem solvatisierten Azid,  $(\text{SO}_2)_n\text{N}_3^-$ , konvertiert, welches im dynamischen Vakuum labil ist und unter  $\text{SO}_2$  Verlust reines  $\text{CsN}_3$  liefert.

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## Introduction

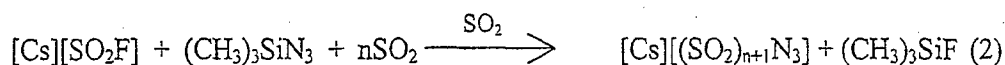
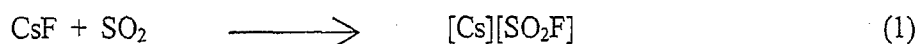
Sodium azide is a widely used reagent and is technically prepared from  $\text{NaNH}_2$  and  $\text{N}_2\text{O}$  [1]. The heavier alkali metal azides are generally prepared starting from  $\text{NaN}_3$ . Two general methodologies for the preparation of heavier alkali metal azides such as  $\text{CsN}_3$  have been employed. The most common preparative route utilizes an aqueous solution of  $\text{HN}_3$  which is neutralized by the corresponding alkali metal hydroxide or carbonate [2-4]. Aqueous  $\text{HN}_3$  is generally prepared from  $\text{NaN}_3$  and  $\text{H}_2\text{SO}_4$  [2]. In the second approach, cesium and rubidium azide have been prepared via ion exchange chromatography starting from aqueous  $\text{NaN}_3$  [5]. Since the handling of  $\text{HN}_3$  is potentially hazardous, a facile synthetic route to  $\text{CsN}_3$  without the use of  $\text{HN}_3$  is highly desirable. Circumventing the use of  $\text{HN}_3$  and laborious chromatographic techniques,  $[\text{N}(\text{CH}_3)_4][\text{N}_3]$  has been prepared from  $[\text{N}(\text{CH}_3)_4][\text{F}]$  and  $(\text{CH}_3)_3\text{SiN}_3$  in  $\text{CH}_3\text{CN}$  solvent [6]. In the present note, we present a new facile laboratory preparation of  $\text{CsN}_3$  starting from  $(\text{CH}_3)_3\text{SiN}_3$  and  $\text{CsF}$  in  $\text{SO}_2$  solvent.

## Results and Discussion

In analogy to the synthesis of  $[\text{N}(\text{CH}_3)_4][\text{N}_3]$ , the preparation of  $\text{CsN}_3$  was attempted from anhydrous  $\text{CsF}$  and excess  $(\text{CH}_3)_3\text{SiN}_3$  in refluxing  $\text{CH}_3\text{CN}$  solvent. The reaction in  $\text{CH}_3\text{CN}$  solvent was found to be slow and did not yield pure  $\text{CsN}_3$  even after five days. The reaction of  $\text{CsF}$  with neat  $(\text{CH}_3)_3\text{SiN}_3$  was also found to be slow; even after three days at temperatures close to the boiling point of  $(\text{CH}_3)_3\text{SiN}_3$  (93 °C) significant amounts of  $\text{CsF}$  were still present. The sluggishness of these reactions is presumably a consequence of the insufficient solubility of  $\text{CsF}$  in  $\text{CH}_3\text{CN}$  and  $(\text{CH}_3)_3\text{SiN}_3$ . The removal of  $(\text{CH}_3)_3\text{SiF}$  and addition of fresh  $(\text{CH}_3)_3\text{SiN}_3$  did not result in a significantly faster conversion, indicating

either the absence of an equilibrium reaction or a coating of the starting material by the product.

Anhydrous CsF reacts with SO<sub>2</sub> solvent to the fluorosulfite anion, SO<sub>2</sub>F<sup>-</sup> (eq. (2)) [7]. The reaction of [Cs][SO<sub>2</sub>F] suspended in SO<sub>2</sub> with excess (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub> results in complete azide-fluoride exchange within less than one hour yielding a clear, yellow solution of [Cs][(SO<sub>2</sub>)<sub>n</sub>N<sub>3</sub>] according to eq. (2).



Removal of the volatiles (SO<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>SiF) at ambient temperature results in precipitation of yellow [Cs][(SO<sub>2</sub>)<sub>2</sub>N<sub>3</sub>] which is converted to [Cs][SO<sub>2</sub>N<sub>3</sub>] and [Cs][N<sub>3</sub>] upon prolonged pumping [8]. Pure [Cs][N<sub>3</sub>] is obtained after SO<sub>2</sub> removal under dynamic vacuum at 55 °C yielding a white solid. Since [Cs][SO<sub>2</sub>F] does not lose SO<sub>2</sub> at 55 °C, the complete conversion of SO<sub>2</sub>F<sup>-</sup> to N<sub>3</sub><sup>-</sup> can be verified by the absence of signals associated with the SO<sub>2</sub>F<sup>-</sup> anion in the Raman spectrum.

## Experimental

**Materials and Apparatus.** All volatile materials were handled in a Pyrex vacuum line equipped with Kontes Teflon valves. Nonvolatile materials were handled in the dry argon atmosphere of a dry box.

The solvents, CH<sub>3</sub>CN (Baker) and SO<sub>2</sub> (Aldrich, >99.9%) were dried over P<sub>4</sub>O<sub>10</sub> and CaH<sub>2</sub> and were freshly distilled prior to use. The CsF (KBI) was fused in a platinum crucible, transferred while hot to the dry box, and finely powdered. Trimethylsilyl azide

(Aldrich, 95%) was purified by fractional condensation through cold traps held at -35 and -196 °C and using the -196 °C fraction.

**Preparation of  $\text{CsN}_3$ .** In a typical reaction, anhydrous  $\text{CsF}$  (2.952 g, 0.0194 mol) was suspended in 8.861 g  $\text{SO}_2$  at room temperature inside a glass vessel equipped with a Kontes valve. Excess trimethylsilyl azide (2.754 g, 0.0239 mol) was condensed onto the frozen reaction mixture at -196 °C. Upon warming to room temperature, the solid phase turned yellow and dissolved in the liquid  $\text{SO}_2$  within 40 min, yielding a two-phase system consisting of a lower yellow and an upper colorless layer. Volatiles were removed under dynamic vacuum at ambient temperatures for approximately 30 min, yielding a yellow solid. Further pumping at 50 to 55 °C for ca. 2 hours yielded pure, colorless  $[\text{Cs}][\text{N}_3]$  (3.400 g; 0.0194 mol).

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